

Supramolecular motifs in 1-(2-cyanoethyl)thymine and 1-(3-cyanopropyl)thymine

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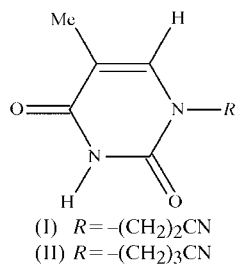
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In both 1-(2-cyanoethyl)thymine [systematic name: 3-(5-methyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-1-yl)propanenitrile], $C_8H_9N_3O_2$, (I), and 1-(3-cyanopropyl)thymine [systematic name: 4-(5-methyl-2,4-dioxo-1,2,3,4-tetrahydropyrimidin-1-yl)butanenitrile], $C_9H_{11}N_3O_2$, (II), the core of the supramolecular structure is formed by centrosymmetric dimers generated by $N-H\cdots O$ hydrogen bonds. Further weak hydrogen bonds of $C-H\cdots O$ and $C-H\cdots N$ types generate molecular tapes and sheets that resemble those in uracil and its methyl derivatives. The steric hindrance that arises from the cyanoalkyl substituents perturbs the conformations of the tapes and sheets.

Comment

In the course of our studies of the hierarchy of intermolecular interactions in crystals (Borowiak *et al.*, 2006; Kubicki *et al.*, 2001, 2002; Kubicki, 2004), the supramolecular structures of two thymine derivatives, *viz.* 1-(2-cyanoethyl)thymine, (I), and 1-(3-cyanopropyl)thymine, (II), have been determined. Both molecules contain a planar thymine ring and, of the several possible tautomeric forms for the ring, the diketo tautomer is observed in the solid state (Figs. 1 and 2). Appreciable differences are observed in the values of the $C=O$ bond



lengths [$C2=O2 = 1.216$ (1) and 1.221 (1) Å for (I) and (II), respectively; $C4=O4 = 1.233$ (1) and 1.237 (2) Å for (I) and (II), respectively]. The existence of two different $C=O$ groups

can be easily rationalized by observing the respective crystal structures.

In (I) and (II), centrosymmetric dimers are formed *via* $N3-H3\cdots O4=C4$ hydrogen bonds. For this reason, $C4=O4$ is longer than the standard carbonyl double bond (Allen, 2002). The second carbonyl group, $C2=O2$, is involved only in weak $C-H\cdots O$ hydrogen bonds (Tables 1 and 2), and this bond is shorter than the $C4=O4$ bond. The geometric perturbation is mainly due to self-association and confirms the fundamental role of conjugative stabilization of the intermolecular hydrogen bonding.

The $C=O$ bond-length pattern in (I) and (II) is in agreement with those in other uracil derivatives. In the structure of (1-thyminyl)acetamide (Borowiak *et al.*, 2006), centrosymmetric dimers are formed *via* $N3-H3\cdots O2=C2$ hydrogen bonds and, in consequence, the $C2=O2$ bond is longer. Similar appreciable discrepancies in the $C=O$ bond lengths have also been found in the structures of uracil (Portalone *et al.*, 1999), thymine (Portalone *et al.*, 1999) or 1-methyluracil (McMullan & Craven, 1989). The hydrogen bonding in the crystal structures of uracil and 1-methyluracil involves atom O4 as acceptor of a strong hydrogen bond but not atom O2. In the structure of 1,3-dimethyluracil, the equivalence of the carbonyl groups is explained by the fact that no $C=O\cdots H-N$ hydrogen bond is possible (Banerjee *et al.*, 1977).

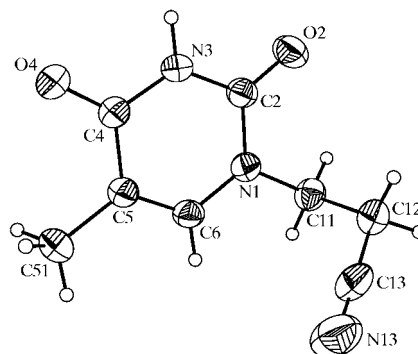


Figure 1
A view of the molecule of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres of arbitrary radii.

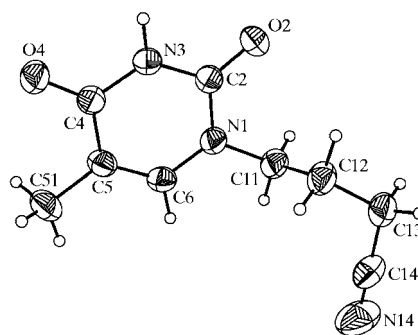


Figure 2
A view of the molecule of (II), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are depicted as spheres of arbitrary radii.

Although the molecules of (I) and (II) differ only by one CH_2 group in the substituent at N1 and intermolecular interactions are of the same type, the supramolecular motifs in their crystal structures differ due to the steric factor determined by the length of the chain. The centrosymmetric dimers form the cores of the supramolecular structures, which are further based on continuous tapes.

In (I), the planar $\text{N3-H3}\cdots\text{O4}$ dimers are connected by $\text{C12-H12B}\cdots\text{O2}$ and $\text{C11-H11B}\cdots\text{O2}$ hydrogen bonds, thus forming the second kind of dimer, a non-centrosymmetric one (Fig. 3*a*). These two consecutive dimers extend to form a molecular tape. On the other hand, two centrosymmetric dimers separated by a non-centrosymmetric one in each tape are set almost perpendicular to one another, giving rise to a sinusoidal shape of tapes; the angle between the planes of two flat dimers is about 78° (Fig. 3*b*).

The tapes are connected in turn by weak $\text{C6-H6}\cdots\text{N13}$ hydrogen bonds. Moreover, the thymine moieties of (I) are mutually oriented in a parallel mode along the shortest unit-cell axis [$b = 4.412$ (1) Å] (Fig. 3*b*). As a consequence of the tape conformation, two different orientations of columns are observed, with the distance between mutually parallel rings being 3.42 (1) Å. The stacking of molecules in (I) occurs with no overlap of pyrimidine rings.

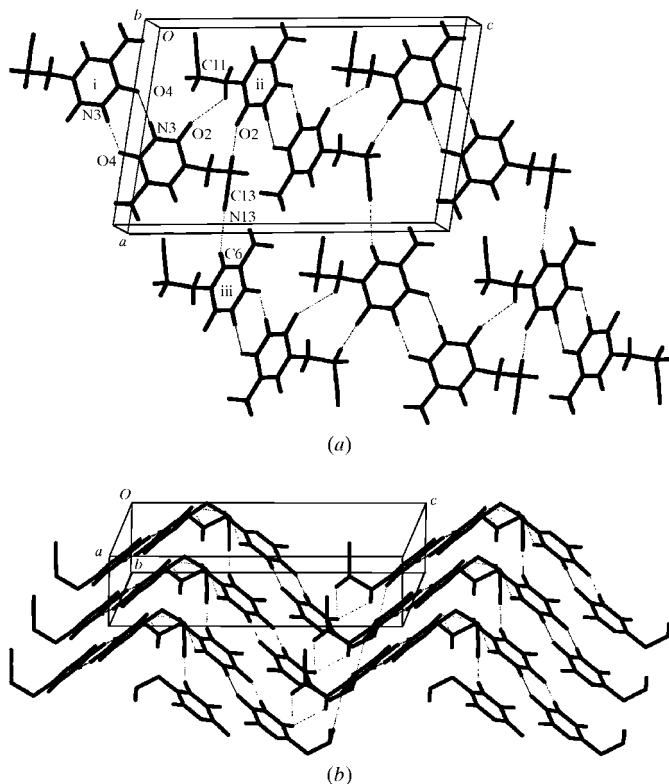


Figure 3
(*a*) The molecular tapes in (I) generated by $\text{N3-H3}\cdots\text{O4}^i$ hydrogen bonds and by weak $\text{C11-H11B}\cdots\text{O2}^{ii}$ and $\text{C12-H12A}\cdots\text{O2}^{ii}$ hydrogen bonds. $\text{C6-H6}\cdots\text{N13}^{iv}$ hydrogen bonds connect the tapes. Hydrogen bonds are indicated by dotted lines. [Symmetry codes: (i) $-x + 1, -y + 2, -z$; (ii) $-x + 1, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-x + 2, \frac{1}{2} + y, \frac{1}{2} - z$.] (*b*) The molecular tapes in (I), expanded along the c axis. A sinusoidal conformation of the tapes is shown. Hydrogen bonds are indicated by dotted lines.

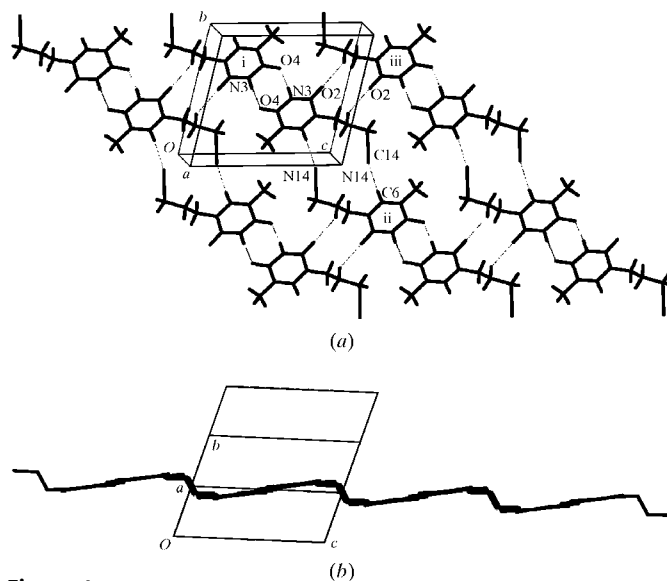


Figure 4
(*a*) The molecular tapes in (II) generated by two consecutive centrosymmetric dimers: one of them *via* $\text{N3-H3}\cdots\text{O4}^i$ and the other *via* weak $\text{C12-H12B}\cdots\text{O2}^{iv}$ hydrogen bonds. $\text{C6-H6}\cdots\text{N14}^{ii}$ hydrogen bonds connect the tapes into sheets. Hydrogen bonds are indicated by dotted lines. [Symmetry codes: (i) $-x, -y + 1, -z + 1$; (ii) $-x + 2, -y, -z + 2$; (iii) $-x, -y + 1, -z + 2$.] (*b*) The molecular tape in (II), expanded along the c axis. Small steps in the tape and sheet conformations are shown.

In (II), the core of the supramolecular structure is also defined by centrosymmetric dimers formed *via* the same type of hydrogen bonds, *viz.* $\text{N3-H3}\cdots\text{O4}$ (Table 2). These dimers are further connected by weak $\text{C12-H12B}\cdots\text{O2}$ hydrogen bonds that form another centrosymmetric dimer (Fig. 4*a*). These consecutive dimers are linked into continuous tapes which are, however, not planar, as small steps are found in their conformation (Fig. 4*b*).

The tapes are further connected into sheets by the third type of centrosymmetric dimer created *via* weak $\text{C6-H6}\cdots\text{N14}$ hydrogen bonds (Fig. 4*a*). The same steps occur in the conformation of the sheets. As in (I), the uracil moieties in (II) also form a parallel mode of packing along the shortest unit-cell axis [$a = 4.859$ (1) Å]. Also in (II), no overlap of the pyrimidine rings is observed.

The features of the supramolecular structures of uracil and its methyl derivatives are retained in compounds (I) and (II), although steric hindrance causes disturbances in the conformations of the tapes and sheets. No carbonyl-carbonyl interactions are found, although this kind of interaction is able to compete successfully with hydrogen bonds (Allen *et al.*, 1998).

Experimental

The synthesis of 1-(3-cyanopropyl)thymine, (II), has been described by Sychala (2000). Crystals of (II) suitable for X-ray data collection were grown from a solution in methanol by slow cooling. 1-(2-Cyanoethyl)thymine, (I), was prepared by the same N-alkylation procedure from thymine and 3-bromopropanenitrile and recrystallized from methanol (m.p. 472–474 K). ^1H NMR (DMSO- d_6 , TMS): δ 1.75 (*s*, 3H, CH_3), 2.88 (*t*, 2H, $J = 6.4$ Hz, CH_2), 3.89 (*t*, 2H, $J = 6.6$ Hz, CH_2), 7.55 (*s*, 1H, C6H), 11.33 (*br s*, 1H, N3H); ^{13}C NMR (DMSO- d_6 , TMS):

δ 11.9, 16.8, 43.0, 99.8, 108.8, 118.8, 150.7, 164.2; FT-IR (KBr, ν_{\max} , cm^{-1}): 3032, 2831, 2245, 1720, 1666, 1480, 1459, 1430, 1389; HRMS (EI): M^+ , found 179.0693; $\text{C}_8\text{H}_9\text{N}_3\text{O}_2$ requires 179.0695. The instrumentation and analysis methods are as described by Spychała (2000).

Compound (I)

Crystal data

$\text{C}_8\text{H}_9\text{N}_3\text{O}_2$ $V = 866.49$ (6) \AA^3
 $M_r = 179.18$ $Z = 4$
 Monoclinic, $P2_1/c$ Mo $K\alpha$ radiation
 $a = 11.2597$ (4) \AA $\mu = 0.10$ mm^{-1}
 $b = 4.4118$ (2) \AA $T = 293$ (2) K
 $c = 17.6256$ (6) \AA $0.45 \times 0.2 \times 0.2$ mm
 $\beta = 98.253$ (3) $^\circ$

Data collection

Kuma KM-4 CCD area-detector 8802 measured reflections
 diffractometer 2187 independent reflections
 Absorption correction: multi-scan 1423 reflections with $I > 2\sigma(I)$
 (*CrysAlis RED*; Oxford $R_{\text{int}} = 0.018$
 Diffraction, 2006)
 $T_{\text{min}} = 0.837$, $T_{\text{max}} = 0.980$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$ 154 parameters
 $wR(F^2) = 0.117$ All H-atom parameters refined
 $S = 1.04$ $\Delta\rho_{\text{max}} = 0.19$ e \AA^{-3}
 2187 reflections $\Delta\rho_{\text{min}} = -0.20$ e \AA^{-3}

Table 1

Hydrogen-bond geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3}\cdots\text{O4}^i$	0.903 (16)	1.929 (17)	2.8301 (14)	174.8 (14)
$\text{C11}-\text{H11B}\cdots\text{O2}^{ii}$	0.972 (15)	2.513 (14)	3.2386 (17)	131.4 (10)
$\text{C12}-\text{H12B}\cdots\text{O2}^{iii}$	0.951 (17)	2.530 (18)	3.4645 (18)	167.6 (13)
$\text{C6}-\text{H6}\cdots\text{N13}^{iv}$	0.933 (14)	2.649 (15)	3.5468 (19)	161.7 (11)

Symmetry codes: (i) $-x+1, -y+2, -z$; (ii) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$; (iv) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

Compound (II)

Crystal data

$\text{C}_9\text{H}_{11}\text{N}_3\text{O}_2$ $\gamma = 80.780$ (11) $^\circ$
 $M_r = 193.21$ $V = 476.94$ (11) \AA^3
 Triclinic, $P\bar{1}$ $Z = 2$
 $a = 4.8591$ (8) \AA Mo $K\alpha$ radiation
 $b = 9.8205$ (12) \AA $\mu = 0.10$ mm^{-1}
 $c = 10.5979$ (11) \AA $T = 293$ (2) K
 $\alpha = 75.815$ (10) $^\circ$ $0.6 \times 0.3 \times 0.1$ mm
 $\beta = 78.364$ (12) $^\circ$

Data collection

Kuma KM-4 CCD area-detector 4787 measured reflections
 diffractometer 2368 independent reflections
 Absorption correction: multi-scan 1842 reflections with $I > 2\sigma(I)$
 (*CrysAlis RED*; Oxford $R_{\text{int}} = 0.011$
 Diffraction, 2006)
 $T_{\text{min}} = 0.969$, $T_{\text{max}} = 1.000$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$ 171 parameters
 $wR(F^2) = 0.121$ All H-atom parameters refined
 $S = 1.07$ $\Delta\rho_{\text{max}} = 0.22$ e \AA^{-3}
 2368 reflections $\Delta\rho_{\text{min}} = -0.24$ e \AA^{-3}

Table 2

Hydrogen-bond geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N3}-\text{H3}\cdots\text{O4}^i$	0.888 (15)	1.932 (16)	2.8165 (12)	173.6 (13)
$\text{C6}-\text{H6}\cdots\text{N14}^{ii}$	0.953 (14)	2.472 (15)	3.4211 (16)	173.6 (11)
$\text{C13}-\text{H13A}\cdots\text{O2}^{iii}$	0.988 (18)	2.557 (18)	3.4751 (19)	154.5 (14)
$\text{C12}-\text{H12B}\cdots\text{O2}^{iv}$	1.010 (16)	2.560 (17)	3.4454 (15)	146.3 (12)

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x+2, -y, -z+2$; (iii) $-x+1, -y+1, -z+2$; (iv) $-x, -y+1, -z+2$.

For both compounds, data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3083). Services for accessing these data are described at the back of the journal.

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